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The Substituent Constants for Some Electrophilic Reactions*

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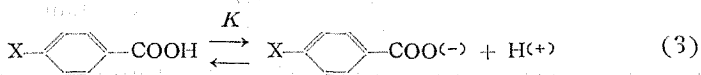
Serious deviations from the Hammett equation are often observed especially in some electrophilic reactions. Swain interpreted these disagreements in terms of his concerted reaction mechanism. Pearson and others proposed corrected values σ_e of the substituent constants for electrophilic reactions. The present author agrees to Pearson's view in that the different sigma values should be required in the reactions of the different type. In this paper a reasonable classification of the reactions is proposed and the validity of this classification is discussed.

The effects of *m*- and *p*-substituents on the rate of aromatic reactions are quantitatively correlated with the Hammett equation:¹⁾

$$\log k/k_0 = \rho\sigma \quad (1)$$

where k_0 is the rate constant of reaction for the unsubstituted compound, k for the substituted compound, and ρ and σ are the reaction- and substituent-constants. As the standard measure of σ , Hammett took the logarithms of the equilibrium constants K of substituted benzoic acids in water at 25°:

$$\log K/K_0 = \sigma \quad (2)$$



Since Hammett derived equation (1) by the analysis of the kinetic data on 52 reactions in which were involved either nucleophilic ($\rho > 0$) or electrophilic ($\rho < 0$) reactions, it appears as if the equation were permitted to fit any aromatic reaction. But it has often been reported that the deviations from the Hammett equation become serious especially in some electrophilic reactions. Swain²⁾ interpreted these disagreements in terms of his concerted reaction mechanism. Pearson and others,³⁾ analyzing the rates of the Beckmann rearrangement of substituted acetophenone oximes, proposed corrected values σ_e of the substituent constants for the electrophilic reactions. The present author agrees to Pearson's view in that the different sigma values should be required in the reactions of the different type.

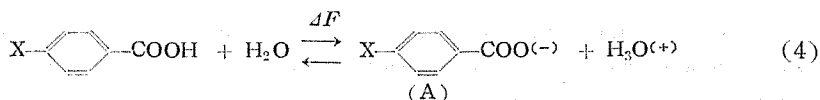
* Partial translation with some revisions of "Substituents and Reactivities" appeared in *Kagaku-no-Ryoiki* (*J. Japan. Chem.*), 8, 209 (1954).

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In this paper a reasonable classification of the reactions is proposed and the validity of this classification is discussed.

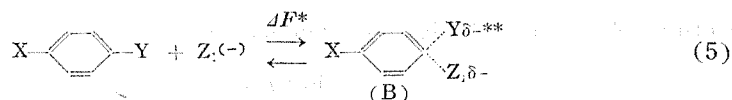
1. CLASSIFICATION OF THE REACTION

For the acid dissociation it is obviously more logical to replace equation (3) by equation (4), because the solvation energy of proton is no doubt the driving force for this dissociation process :



where ΔF is the free energy change between the two systems. The solvation for the neutral molecule or the anion is probably negligibly small compared with that for proton.

In a nucleophilic reaction, an equilibrium should be set up between the initial and the activated states in such a way as



where $\text{Z}_1^{(-)}$ is an anion and ΔF^* is the free energy of activation of the nucleophilic reaction. Since (B) as well as (A) has a negative charge, a parallelism between the effects of the substituents in reactions (4) and (5) is expected. The situation can be expressed as

$$\left(\frac{\partial \Delta F^*}{\partial x} \right) / \left(\frac{\partial \Delta F}{\partial x} \right) = \text{constant} \quad (6)$$

where ∂x represents a change in the effect of substituents. Therefore, the term $\frac{\partial \Delta F}{\partial x}$ is evidently equivalent to the Hammett ρ constant.

In these reactions the reaction constant rho is positive ($\rho > 0$). If the substituent Y or Z_1 conjugates with X in a way different from that in which COOH or $\text{COO}^{(-)}$ does, equation (6) should fail to be valid. Dual sigma values of nitro group and some electron attractive groups suggested by Hammett are probably due to the different conjugation between the substituents.

In an electrophilic reaction, the conjugation is completely different from that in reaction (4), because an activated complex (C) carries a positive charge contrary

** The electronic structure of the aromatic ring of the complex (B) should differ from that of the initial state. However, since few of the proposed electronic expressions for the activated complex seem to be satisfactory, a classical formula (B) was adopted, close discussions for the electronic structure of the complex being not within the purpose of this paper.



Enhanced deviations from the Hammett sigma were observed in the reactions in which the solvation energy of the activated complex was one of the most important chemical driving forces of the reaction. The solvolysis of the benzyl chlorides is considered to proceed according mainly to the S_N1 mechanism. The solvation is probably affected by the conjugated state of the complex. A bulky group, as Price suggested,²⁰ may inhibit the orientation of the solvent to decrease energy. Since the activation entropy of the reaction is markedly affected with the degree of solvation, the constancy of the linearity of the activation entropy against the activation energy can hardly be expected in this solvolysis. Furthermore, it cannot be decided that the solvolysis of the benzyl chlorides may proceed along the same mechanism irrespective of the nature of the substituent.

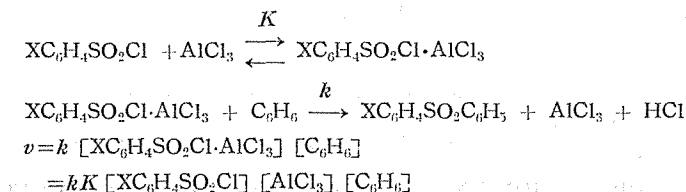
$$\left\{ \begin{array}{l} 1. \text{ nucleophilic reactions} \quad (\sigma \text{ is applicable}) \dots\dots\dots (A) \\ 2. \text{ electrophilic reactions} \left\{ \begin{array}{l} \text{incapable of conjugating } (\sigma \text{ is applicable}) \dots\dots\dots (B) \\ \text{capable of conjugating } (\sigma_e \text{ is applicable}) \dots\dots\dots (C) \end{array} \right. \end{array} \right.$$
$$\text{Y}-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2 + \text{RX} \longrightarrow \left[\text{Y}-\text{C}_6\text{H}_4-\overset{(-)}{\underset{\text{R}}{\text{N}}}(\text{CH}_3)_2 \right] \text{X}^{(-)} \quad (8)$$


In these reactions, it is very likely that the nitrogen atom in the transition state becomes more positive than in the initial state. Thus, the more electron-repulsive the substituent Y, the better stabilized will be the activated complex ($\rho < 0$). Since the ammonium ion, on the contrary to the carbonium ion, is incapable of conjugating with electron-donating group such as methoxyl or dimethylamino group, the reaction (8) should fall under the group (B). In a similar way, it is easily understood that the 3 reactions involving phenolate ions also belong to group (B).

Acid catalyzed hydrolysis of the benzyl acetates and of the phenyl acetates seems to follow the Hammett equation with negative rho values, but the influences of the substituents in the rate of reaction are so small ($\rho: -0.053$ for the benzyl ester; $\rho: -0.134$ for the phenyl ester) that it is not considered reasonable to discuss immediately the rate of reaction in connection with the polarity of the substituents. For instance, according to the original data, the rate of hydrolysis of *m*-nitrophenyl acetate is 0.5 kcal smaller than that of the unsubstituted in spite of the smaller activation energy of the former, the *PZ* term determining the rate of these reactions.

The hydrolysis of the benzyl chlorides in aqueous acetone solution mainly proceeds along the S_N1 mechanism where a contribution of the solvation as well as the conjugation may become significant as stated above. In actuality, a plot of the original data²⁾ showed a marked deviation of methyl group from the Hammett equation.

Hammett cited a series of the Friedel-Crafts reactions in which the rates v of reaction of the parasubstituted aromatic sulfonyl chlorides on benzene were determined. It is becoming widely believed that the mechanism of the Friedel-Crafts reaction is as follows:



Since it is evidently not k but kK that is obtainable from the original data,²⁾ the immediate comparison of kK with σ should not be regarded as logical. It is to be noted that the Friedel-Crafts reactions cited by Hammett were not the substitution reactions of an organic chloride towards substituted benzenes. Olivier presented the kinetics for the latter case,³⁾ but his data also are not quite satisfactory for more precise arguments, because each reaction was not carried out in the same solvent.

The 3 reactions with $\rho < 0$, which were not discussed above, are lacking in the

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data for substituents of sufficient number and the reaction mechanisms are not clear.

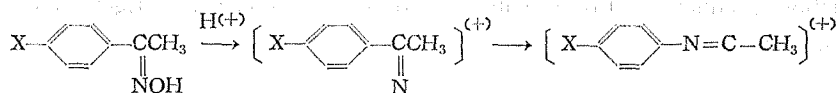
Hammett illustrated the validity of the application of his value for an aromatic nitration which is widely believed to be one of the typical electrophilic reactions. However, the points corresponding to the σ values smaller than -0.2 , about which are expected marked deviations, are not involved in his plot.

Since the Hammett σ values are examined by the 52 kinds of reaction involving not only the nucleophilic reactions but also the electrophilic ones such as nitration or Friedel-Crafts reaction, one may suppose the Hammett σ may fit any reactions concerning *m*- and *p*-substituted aromatic compounds. But, from the above discussion, it can be understood that a large variety of reactions deviating from the Hammett σ constants is also present in the aromatic reactions.

3. REACTIONS TO BE INCLUDED IN THE GROUP C

i. Some Molecular Rearrangement

a. Beckmann rearrangement. Pearson and others³⁾ proposed another series of sigma values σ_e for the electrophilic reactions. They used the Beckmann rearrangement for the calculation of the corrected sigma values σ_e . The rate determining step of the reaction is regarded as



In the activated complex of this reaction, a stabilization owing to the conjugation with X grouping is expected if the latter is an electron donating group. Thus, the rearrangement is considered to be included in C group. Pearson's tabulation is reproduced in Table 1, in which the notation σ_e instead of σ_c is used.

Table 1

Substituent	σ_e	Hammett σ
H	0	0
<i>p</i> -CH ₃	-0.138	-0.170*
<i>p</i> -CH ₃ O	-0.54	-0.268
<i>p</i> - <i>t</i> -Bu	-0.128	-0.199
<i>p</i> -Cl	0.10	0.227
<i>p</i> -NO ₂	0.778	0.778

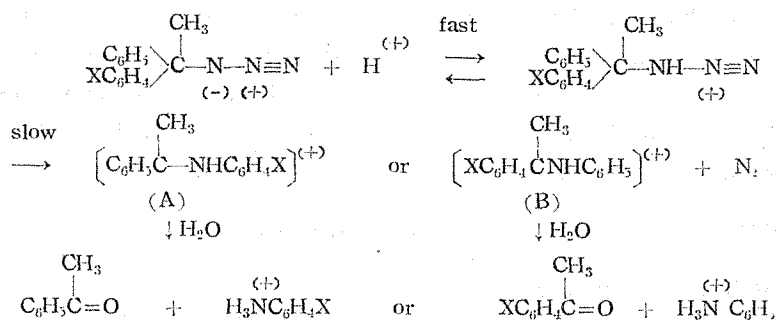
* In Pearson's paper the value is erroneously written.

There seems to be considerable roughness in the σ_e values thus obtained, as Pearson himself admitted, but the pronounced variation found in group *p*-CH₃O is to be noted in comparison with its enhanced ability of the conjugation.

b. Pinacol rearrangement. Many studies dealing with the pinacol rearrangement indicated large departures of the methoxyl grouping from the linear relation-

ship, the rate of the methoxyl derivative being reported 500 times as large as that of the unsubstituted. But this divergency is considerably improved by using σ_e .

c. **Schmidt rearrangement.** Ege and Sher¹⁰) studied the Schmidt rearrangement of the azides which were prepared by acting hydrazoic acid upon the asymmetrically substituted diaryl ethylenes. The reaction is considered to proceed along the following mechanism :



The rate determining step of the reaction is most likely to be that of the nitrogen evolution. As it is seen in the above scheme, the migratory aptitude of the substituted phenyl relative to the unsubstituted can be known from the analysis of the reaction products. From Table 2, No. 1, it is seen that Ege's data strictly fit σ_e , but not σ .

Table 2. Partial list of reactions to be included in the group C ^(a).

No.	Reaction	Correlation with σ			Correlation with σ_e		
		ρ	s ^(b)	r ^(c)	ρ_e	s_e ^(b)	r_e ^(c)
1,	Schmidt Reaction	-3.99	0.605	0.769	-2.39	0.059	0.998
2,	Stannic-chloride-catalyzed copolymerization of $\text{C}_6\text{H}_5\text{C}=\text{CH}_2$ with $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$	-3.93	0.640	0.745	-2.43	0.043	0.999
3,	Radical copolymerization of $\text{CH}_2=\text{CH}-\text{COOCH}_3$ with $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$	-0.452	0.108	0.596	-0.333	0.041	0.954
4,	Radical copolymerization of $\text{CHCO} \begin{array}{c} \diagup \text{O} \\ \diagdown \end{array} \text{CHCO}$ with $\text{XC}_6\text{H}_4\text{C}=\text{CH}_2$	-3.58	0.740	0.656	-2.47	0.098	0.995

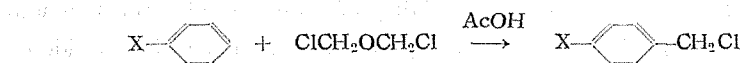
^(a) Reactions No. 2, 3 and 4 are calculated with the substituents $p\text{-N}(\text{CH}_3)_2$, $p\text{-CH}_3\text{O}$, $p\text{-CH}_3$, $p\text{-H}$ and $p\text{-Cl}$; Reaction No. 1. with $p\text{-CH}_3\text{O}$, $p\text{-CH}_3$, $p\text{-H}$ and $p\text{-Cl}$.

^(b) Standard deviation.

^(c) Correlation coefficient of the regression line.

ii. Chloromethylation.

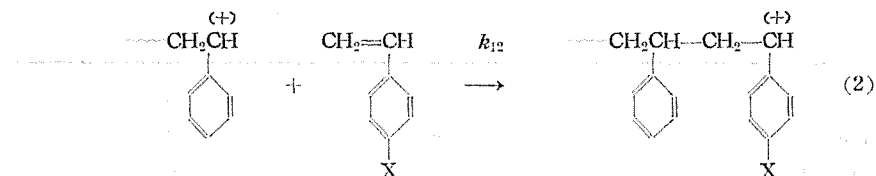
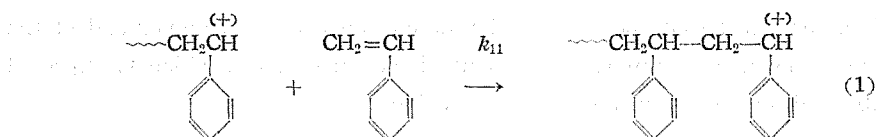
Chloromethylation is considered a weak electrophilic reaction. From the examination of the reaction ⁽¹¹⁾



it was made clear that σ_e was also true for this reaction.

iii. Electrophilic Polymerizations

a. Cationic polymerizations. From the stannic chloride-catalyzed copolymerizations of the substituted styrenes with styrene, *p*-chlorostyrene or *o*-methylstyrene, Overberger and others ⁽¹²⁾ determined reactivities of the substituted styrenes towards styrene-, *p*-chlorostyrene- and *o*-methylstyrene-carbonium ions, respectively.



The rate constants of reactions (1) and (2) are denoted by k_{11} and k_{12} . The reactivities of the double bonds towards the terminal styrene cation of the growing polymer are generally represented in terms of the monomer reactivity ratio, $r_1 = k_{11}/k_{12}$, the values of which are obtainable from the experiment. The relative rates of the substituted styrenes in the copolymerization are expressed by the reciprocal of the monomer reactivity ratio ($1/r_1$). Significant departures of methoxyl and dimethyl-amino-group from the linearity are again observed in the cationic copolymerization. These disagreements are to be expected from the discussion presented above. From Table 2-No. 2, it can be seen that the corrected values σ_e still hold well with this reaction. Corrected sigma value of $-\text{N}(\text{CH}_3)_2$ group applicable to this reaction has been found to be -0.97 which is in good accord with one of the values given in Jaffe's paper. ⁽¹³⁾

b. Radical copolymerization. Walling and others, ^{(14), (15)} from the copolymerization data, examined the reactivities of para substituted styrenes towards some radicals. They found that the Hammett plot for the styrene radical gave a fairly good straight line ($\rho > 0$), whereas the corresponding plot for the methacrylate radical did not. A serious disagreement with the Hammett σ constant was again observed in the relative reactivities of the substituted *o*-methyl styrenes towards the maleic anhydride radical. These divergencies for methacrylate and maleic radicals appear entirely

irregular, but close examination on the data reveals the relative reactivities to be irregular with the electron donating substituents, the reaction constant being negative ($\rho < 0$). Therefore, in these reactions the corrected values σ_c may be used for the Hammett plot. Table 2-No.3 and 4 show the validity of these considerations though the significant deviation of *p*-CN is not reasonably accounted. It can be considered that the rates of reaction with the styrene radical are in good accordance with the Hammett σ owing to its nucleophilic or donating nature ($\sigma > 0$) towards the vinyl monomer.

From the above discussion, it is supposed that the electrophilic ($\rho < 0$) radical as well as the nucleophilic radical ($\rho > 0$) can be present. In this connection, Price-Alfrey's *Q-e* scheme or Furukawa's *J-e* values seem to be of much interest. Price-Alfrey's *e*-values represent the polar nature of the double bond in vinyl monomers. It is assumed that the *e*'s of the double bond of a monomer and of the radical arising from it are similar. A parallelity between *e* and ρ , which is expected from the above discussion, can be seen from Table 3.

Table 3.

	<i>e</i>	ρ
Styrene	-0.8	0.51
Methacrylate	0.3	-0.333
Maleic anhydride*	1.5	-2.47

* the *e*-value of diethyl fumarate

The agreement seems to be satisfactory considering the natures of *e* and ρ .

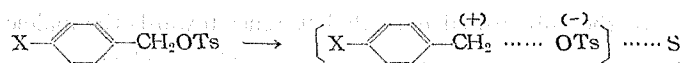
4. THE REACTIONS OF THE BENZYL DERIVATIVES

More serious deviations of methoxyl and methyl groups were observed in the solvolysis of the benzyl tosylates. Kochi and Hammond⁽¹⁵⁾ proposed sigma constants characteristic to this solvolysis:

Substituent	σ_{tosylate}	σ	$\Delta\sigma$
<i>p</i> -CH ₃ O	-2.5	-0.27	-2.2
<i>p</i> -CH ₃	-0.63	-0.17	-0.46

The present author confirmed σ_{tosylate} to be applicable to the solvolysis of the benzyl chlorides.

It is widely recognized that the solvolysis of the benzyl chlorides or tosylates mainly proceeds along the S_N1 mechanism:



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where S denotes the solvent used. The driving force of the reaction is the solvation energy in the transition state. The serious deviations of methoxyl and methyl groups appear to arise from the various factors as stated above, though detailed picture is still obscure.

5. JAFFÉ'S REEXAMINATION

Recently Jaffé presented an extensive reexamination on the Hammett equation. In Tables 1 and 2 of his paper, the reaction series applicable to the equation are tabulated. It is seen from the Tables that, of 418 reaction series, only 167 * have negative reaction constants.

The validity of the foregoing considerations is again ascertained by a simple statistical treatment of Tables 1 and 2 :

Table 4.

Standard deviation	Reactions with $\rho > 0$	Reactions with $\rho < 0$
0.000 - 0.100	54.1 %	51.5 %
0.101 - 0.200	31.9	22.7
0.201 - 0.300	9.8	13.7
0.301 - 0.400	3.7	7.7
0.401 - 0.500	0.5	1.4
0.501 - 0.600	0.0	3.0

Larger deviations from the straight line are seen obviously in the reaction series with negative reaction constant ($\rho < 0$). It is to be noted that compounds involving dimethylamino-group are excluded from Jaffé's calculation. The deviations will undoubtedly become much more serious, especially in reactions belonging to group C, if dimethylamino group is taken into the calculation.

The standard deviations are larger than 0.301 in the 20 reaction series with negative ρ values, in which electrophilic copolymerizations, S_N1 solvolysis, and nitration are involved. The reasonable explanation for these deviations were discussed above. Serious departures in the acid-catalyzed shifts of the double bond are also interpreted in a similar way. The same phenomena are also considered as responsible for abnormally small values of the correlation coefficients, for examples, those for reaction No. 93, 197, 198 or 199.

Acknowledgment. The author wishes to express his sincere thanks to Professors R. Oda and J. Furukawa for their helpful discussions and encouragement in the study.

* The value for the reaction number 96 is misprinted, the reaction evidently having negative ρ value.

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